

# DIELECTRIC BEHAVIOURS OF PEO-LiCF<sub>3</sub>SO<sub>3</sub> ELECTROLYTES

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## Abstract

*Polymer electrolyte composed of poly (ethylene oxide) as a host polymer and LiCF<sub>3</sub>SO<sub>3</sub> as salt was studied. Different compositions of PEO-LiCF<sub>3</sub>SO<sub>3</sub> electrolytes were prepared by solution casting technique. Measurement of conductivity and dielectric properties were carried out on these films as a function of frequency at various temperatures. The highest conductivity obtained was  $7.75 \times 10^{-8}$  S/cm for a ratio of 80 wt% PEO: 20 wt% LiCF<sub>3</sub>SO<sub>3</sub>. The relaxation time,  $\tau$  for the ionic charge carriers, was obtained from the variation of loss tangent ( $\tan \delta$ ) with frequency for the highest conductivity value. The linear behavior of temperature dependence of the complex film appears to obey the Arrhenius Law. The activation energy for the highest conductivity PEO-LiCF<sub>3</sub>SO<sub>3</sub> sample was found 0.74 eV.*

**Keywords:** poly (ethylene oxide), LiCF<sub>3</sub>SO<sub>3</sub>, conductivity, relaxation time, dielectric

## 1. Introduction

Current research trends have been concerned with lithium salt-based polymer electrolytes (Manning et al., 1990; Gauthier et al., 1989) due to their potential applications in batteries (Frech et al., 1996; Gray, 1991), with a particular interest in the development of novel polymer electrolytes with high ionic conductivities at ambient temperature. PEO in particular is an exceptional polymer which dissolves in a wide variety of salts to form polymeric electrolytes. The chemical stability of the ether functional group strengthens the superiority of PEO as a host for a solid polymer electrolyte (Chandrasekaran et al., 2001; Armand, 1987). In this paper, the author reports the conductivity values and the dielectric behaviour of thin polymer electrolyte film based on PEO and LiCF<sub>3</sub>SO<sub>3</sub> salt.

## 2. Method

The polymer electrolytes in this study were prepared by the solution cast technique. In this method, AR grade PEO (Aldrich, average molecular weight ca. 600,000 g/mol) and a suitable amount of lithium salt (lithium triflate, LiCF<sub>3</sub>SO<sub>3</sub> – Aldrich) were dissolved in methanol at 50 °C and room temperature (RT) respectively. PEO with molecular weight 600,000 g/mol was used due to its high molecular weight to make sample more stable. The amount of PEO in this work was fixed at 1 g and was stirred at 50 °C since at this temperature, this PEO was completely dissolved.

The solutions were mixed and stirred for 24 hours at 50 °C. The mixture was then cast into Teflon petri dishes and allowed to evaporate slowly at RT to form films of about 0.05 mm thick. The films were then kept in a dessicator for a week for further evaporation. The resulting films were then cut into a circle of 24 mm diameter and the thickness of every sample was measured. The dried samples were then characterized by impedance spectroscopy using the HIOKI 3532-50 LCR HiTESTER. The prepared films were cut into suitable sizes and sandwiched between

two circular stainless steel ion-blocking electrodes. The study was carried out in the frequency range from 100 Hz to 5 MHz. The conductivity was calculated using the relation:

$$\sigma = t/AR_b \quad (1)$$

where  $\sigma$  is the conductivity,  $t$  is the thickness of the film,  $A$  is the area of contact, and  $R_b$  is the bulk resistance of the sample in  $\Omega$  which is obtained from the complex impedance plot.

### 3. Results and Discussions

The impedance plot of pure PEO film is shown in Figure 1. It is observed that the impedance plot consists of part of a depressed semi-circle with no spike. The bulk resistance,  $R_b$  is obtained from this plot by taking the intercept at the  $Z_r$  axis. The RT electrical conductivity of pure PEO is then calculated from equation 1 and gives an average value of  $4.43 \times 10^{-11}$  S/cm.

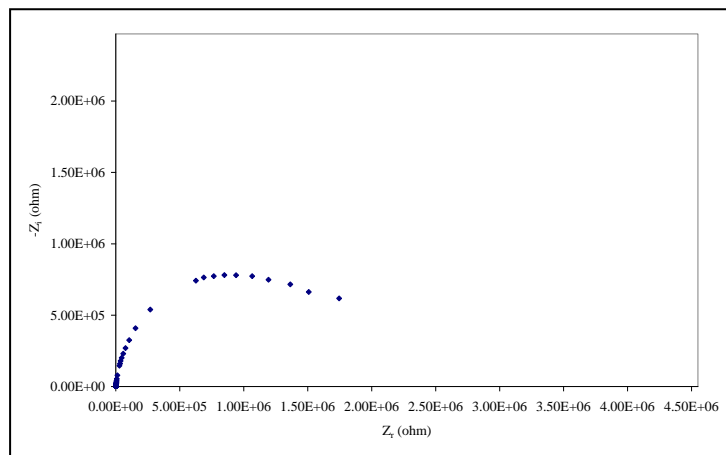


Figure 1. Impedance plot of pure PEO film.

The highest conductivity of PEO-LiCF<sub>3</sub>SO<sub>3</sub> system was obtained at 20 wt.% of LiCF<sub>3</sub>SO<sub>3</sub> which is  $7.75 \times 10^{-8}$  S/cm at RT. The impedance plot of this sample is shown in Figure 2. In this plot part of a semi-circle at the high frequency end and a spike at the low frequency end is observed. According to Benedict et al., (1998), the high frequency semicircle yields information about the properties of the electrolyte such as bulk resistance,  $R_b$  and bulk capacitance,  $C_b$  which arise from the migration of lithium ions. The appearance of the semi-circle with a low frequency tail (spike) in Figure 2 indicates the capacitive nature of the interface and the absence of electronic conductivity in the cell (Michael et al., 1997).

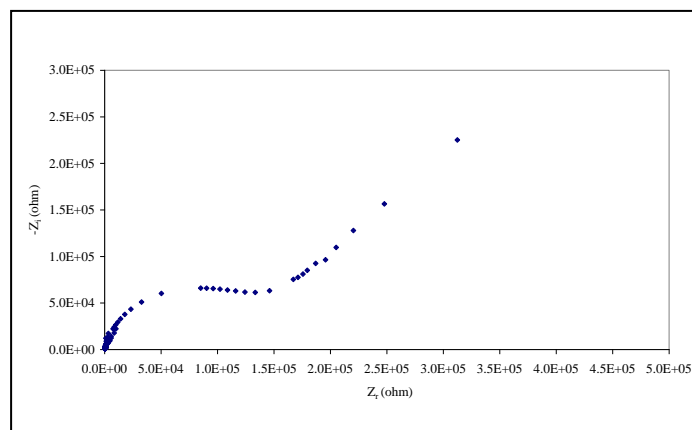


Figure 2. Impedance plot of ionic conductivity for the highest conducting system PEO-LiCF<sub>3</sub>SO<sub>3</sub> (PLT20) film

Table 1 shows the average RT ionic conductivity for the various compositions of PEO-LiCF<sub>3</sub>SO<sub>3</sub> complexes prepared while Figure 3 depicts the variation of the average RT ionic conductivity as a function of LiCF<sub>3</sub>SO<sub>3</sub> concentration. As mentioned earlier, the highest conductivity of the system was obtained for the film with 20 wt.% of LiCF<sub>3</sub>SO<sub>3</sub>. This is due to the increase in the number of charge carriers and in the increase in their mobility with addition of LiCF<sub>3</sub>SO<sub>3</sub>. Above 20 wt.% of LiCF<sub>3</sub>SO<sub>3</sub> the conductivity decreases due to the presence of a large number of ions.

Table 1. Average conductivity values of PEO-LiCF<sub>3</sub>SO<sub>3</sub> system at room temperature.

Sample	PEO-LiCF <sub>3</sub> SO <sub>3</sub> (wt.%)	Average ionic conductivity (S/cm)
PLT05	95:05	8.12 x 10 <sup>-9</sup>
PLT10	90:10	9.72 x 10 <sup>-9</sup>
PLT15	85:15	5.87 x 10 <sup>-8</sup>
PLT20	80:20	7.75 x 10 <sup>-8</sup>
PLT25	75:25	4.93 x 10 <sup>-8</sup>
PLT30	70:30	4.00 x 10 <sup>-8</sup>

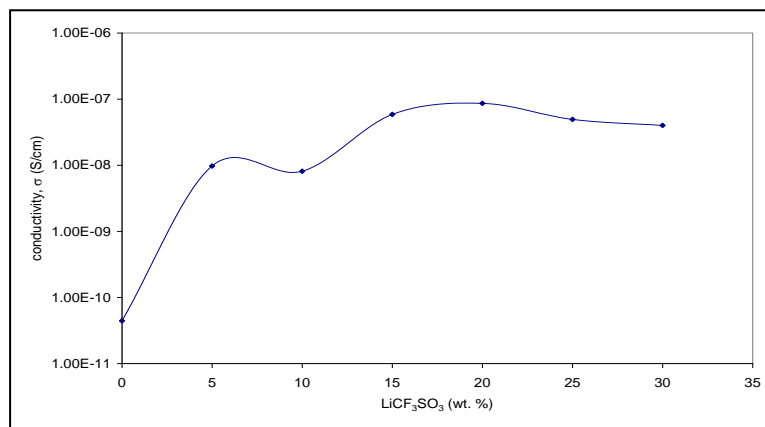


Figure 3. Variation of conductivity for PEO with different wt% LiCF<sub>3</sub>SO<sub>3</sub>

Figure 4 shows the dependence of conductivity on temperature for PLT20 system in the temperature range 300 – 333 K. The straight line fit of the conductivity with temperature indicates an Arrhenius type of behaviour with regression value 0.98. The activation energy for the system is obtained using the equation:

$$\sigma = \sigma_0 \exp(-E_A/kT) \quad (2)$$

where  $\sigma_0$  is the pre-exponential factor,  $E_A$  is the activation energy,  $k$  is the Boltzmann constant and  $T$  is temperature in Kelvin. The activation energy for PLT20 system was found to be 0.74eV.

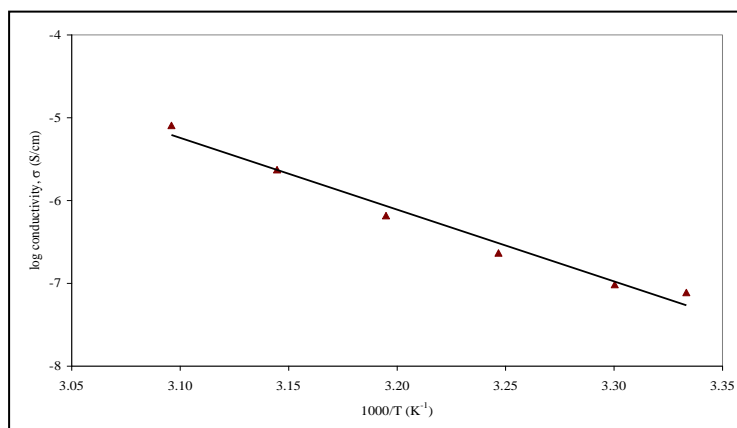


Figure 4. Temperature dependence of PLT20 sample

Figure 5 depicts the variations of dielectric constant and dielectric loss at different temperatures for PLT20. Both of the  $\epsilon_r$  and  $\epsilon_i$  rise sharply at the low frequency end and is displaced towards higher frequencies at higher temperatures. This can be explained by the movement of charge carriers. At relatively low temperature, the charge carriers cannot orient themselves with respect to the direction of the applied field. Therefore, they possess a weak contribution to the polarization and the dielectric constant. As the temperature increases, the bound charge carriers get enough excitation from thermal energy to be able to obey the change in the external field more easily. This in turn enhances their contribution to the polarization leading to an increase in the dielectric constant of the sample (Abo El Ata, 2004).

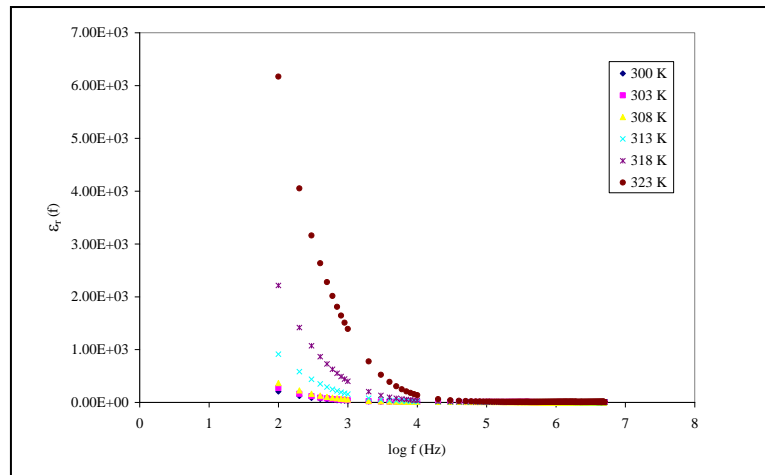


Figure 5(a). Dielectric constant versus frequency for PLT20 at different temperature.

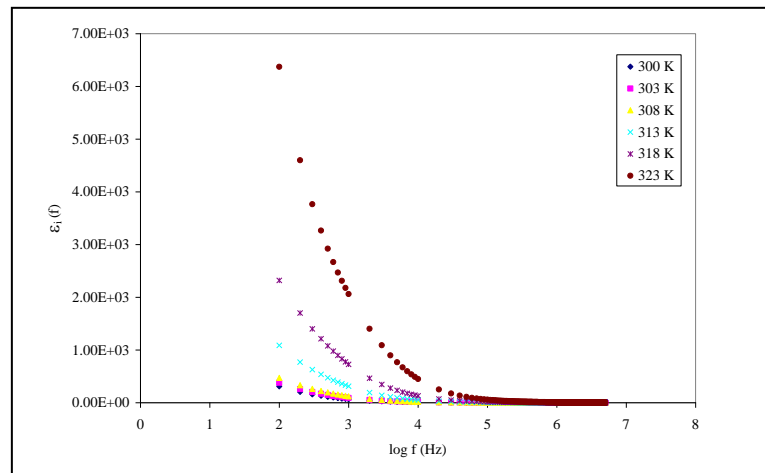


Figure 5(b). Dielectric loss versus frequency for PLT20 at

Figure 6 shows the variation of real part and imaginary part of electrical modulus for PLT20 system. It can be observed that at higher frequencies,  $M_r$  value is found to increase gradually with a tendency for saturation. The observed dispersion is mainly due to conductivity relaxation spread over the range of frequencies studied. The low values of  $M_i$ , in the low frequency region indicates negligible contribution of electrode polarization to the electric modulus (Bhide & Hariharan, 2007). Also apparent, is the dispersion of both  $M_r$  and  $M_i$  values at the rising portion of the curves.

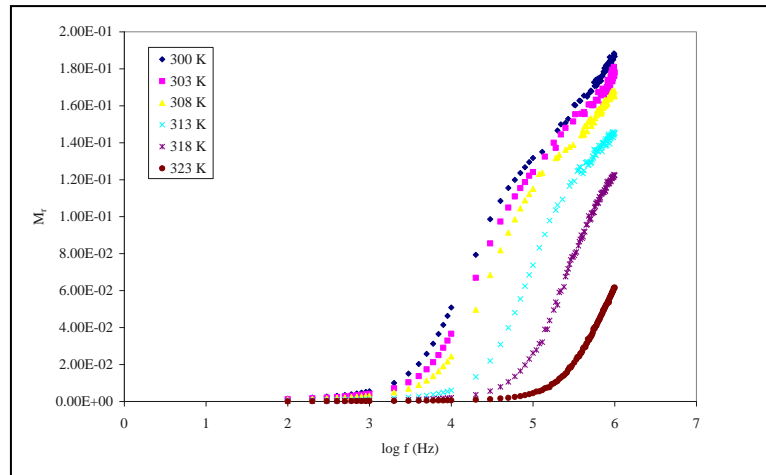


Figure 6(a). Real part of electrical modulus versus frequency for PLT20 at different temperature.

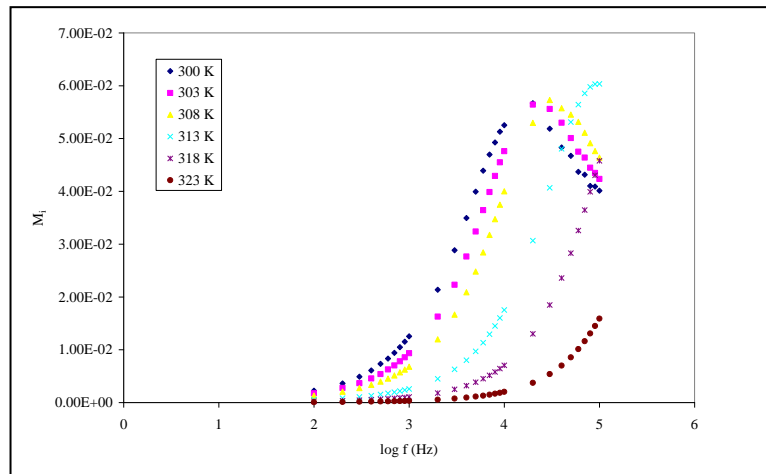


Figure 6(b). Imaginary part of electrical modulus versus frequency for PLT20 at different temperature.

The variation of  $\tan \delta$  as a function of frequency at various temperatures for PLT20 is shown in Figure 7. This is plotted in order to study the relaxation time for ionic charge carriers. It is clearly observed that  $\tan \delta$  increases with frequency, pass through a maximum value and thereafter decreases. As the temperature is increased, the frequency at which  $(\tan \delta)_{\max}$  occurred shifted to higher frequencies and at the same time the height of  $(\tan \delta)_{\max}$  also increased. The occurrence of relaxation time,  $\tau$  can be obtained from the peak of  $\tan \delta$  using the relation:

$$\tau = 1 / \omega_{\text{peak}} \quad (3)$$

where  $\omega = 2\pi f$  and  $f$  is the frequency of the relaxation peak. The relaxation time for PLT20 at selected temperature is listed in Table 2. From the table, it can be observed that as temperature increased, the relaxation time is decreased, implying that as temperature increased the ions hop/migrate faster, thus confirming the Arrhenius plots obtained earlier.

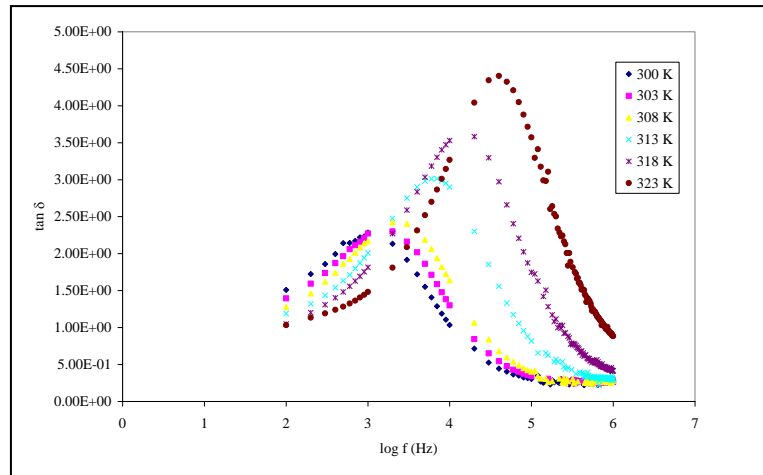


Figure 7. Variation of loss tangent ( $\tan \delta$ ) with frequency for PLT20 at different temperature.

Table 2. Relaxation time at selected temperatures for PLT20

Temperature (K)	$\tau$ (s)
308	$7.96 \times 10^{-5}$
313	$2.27 \times 10^{-5}$
323	$3.98 \times 10^{-6}$

#### 4. Conclusion

The highest conductivity of PEO-LiCF<sub>3</sub>SO<sub>3</sub> system was obtained at 20 wt.% of LiCF<sub>3</sub>SO<sub>3</sub> which is  $7.75 \times 10^{-8}$  S/cm. The temperature dependence of PEO-LiCF<sub>3</sub>SO<sub>3</sub> system for PLT20 shows Arrhenius behaviour with regression value 0.98 which confirm that the dielectric behaviour of the prepared sample show strong dependence on frequency.

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